

Pre-K-Edge Structure on Anomalous X-Ray Scattering in LaMnO_3

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We study the pre-K-edge structure of the resonant X-ray scattering for forbidden reflections (anomalous scattering) in LaMnO_3 , using the band calculation based on the local density approximation. We find a two-peak structure with an intensity approximately 1/10 of that of the main peak. This originates from a mixing of $4p$ states of Mn to $3d$ states of neighboring Mn sites. The effect is enhanced by an interference with the tail of the main peak. The effect of the quadrupole transition is found to be one order of magnitude smaller than that of the dipole transition, modifying slightly the azimuthal-angle dependence.

KEYWORDS: resonant X-ray scattering, LaMnO_3 , pre-peak of the K-edge, quadrupole transition, cooperative Jahn-Teller effect, orbital ordering

Resonant X-ray scattering technique has recently attracted much interest as a method of observing orbital order. Murakami *et al.*¹⁾ carried out such an experiment with photon energy around the K-edge of Mn in LaMnO_3 , and found that the forbidden $(h, 0, 0)$ reflection with h being an odd integer gains some intensity below 780K, where the crystal starts to distort.¹⁾ We call this phenomenon anomalous X-ray scattering (AXS). The relevant states are $4p$ states of Mn. They are highly extended in the crystal. Therefore this AXS intensity does not directly reflect orbital order. Ishihara and Maekawa²⁾ suggested that the energy levels of $4p_x$ and $4p_y$ states are split by the anisotropic part of the intraatomic Coulomb interaction between $4p$ and $3d$ states and that its dependence on occupied orbitals $d_{3x^2-r^2}$ or $d_{3y^2-r^2}$ causes the AXS intensities. However, Elfimov *et al.*,³⁾ Benfatto *et al.*⁴⁾ and the present authors⁵⁾ have recently carried out *ab-initio* calculations, and have explicitly shown that neighboring oxygens strongly influence the $4p$ states of Mn through a Jahn-Teller (JT) distortion, resulting in a large AXS intensity. Those authors have also shown that the intraatomic Coulomb interaction has a small effect on the AXS intensity only.^{3, 4, 5)}

The above studies refer to AXS near the main peak. Recently, pre-K-edge (PKE) structures have been observed in the AXS intensity in other materials such as V_2O_3 ⁶⁾ and in resonant magnetic X-ray scattering in CoO .⁷⁾ In this paper we focus our attention on the PKE structure of the AXS intensities in LaMnO_3 . Although it has not been observed yet, we hope that this study encourages experimentalists to investigate the PKE structures in that material.

On each Mn atom in LaMnO_3 , the doubly-degenerate e_g orbitals are occupied by one electron only [$(t_{2g})^3(e_g)^1$ configuration because of the cubic symmetry]. Spins of the $3d$ electrons are parallel on each atom due to a strong Hund-rule coupling, and show antiferromagnetic long-range order.⁸⁾ The orbital degeneracy is lifted by a JT

distortion, which takes place cooperatively in a crystal,⁹⁾ or by the orbital exchange interaction, which is similar to the superexchange for spins.¹⁰⁾ Independent of the particular driving force, a sizable crystal distortion is realized. In the actual crystal, the structure is more complicated because each MnO_6 octahedra is slightly tilted, implying a P_{nma} structure.¹¹⁾ For the crystal distortion of LaMnO_3 , see Fig. 1 in Ref. 5.

Fig. 1. Occupied (hatched lobes) and unoccupied (open lobes) e_g orbitals for the majority spin states. Orbitals are “antiferromagnetically” ordered in the $a-b$ plane and “ferromagnetically” ordered along the c axis. Solid circles represent oxygen atoms.

We carry out a band calculation based on the local-density approximation (LDA) and the use of the KKR method, just the same way as in Ref. 5, assuming the actual crystal distortion and tilt. As a result, we obtain an insulating ground state with a gap of ~ 0.2 eV (experimentally ~ 0.24 eV¹²⁾). Spins align ferromagnetically in the $a-b$ plane and antiferromagnetically along the c axis (A-type antiferromagnet), with a magnetic moment of $3.35 \mu_B$ per Mn atom. Orbitals are ordered “antiferromagnetically” in the $a-b$ plane and “ferromagnetically” along the c axis. These findings are consistent with ex-

periments. In case of orbital order, Mn sites are divided into two sublattices A and B such that at A sites the $d_{3x^2-r^2}$ state has a larger occupation number than the $d_{y^2-z^2}$ state. Figure 1 shows schematically this situation. The present calculation gives for the occupation numbers of the $d_{3x^2-r^2}$ and $d_{y^2-z^2}$ orbitals the values 0.92 and 0.57, respectively, in fair agreement with previous calculations.¹³⁾

Figure 2 shows the density of states (DOS) projected onto states of d symmetry above the top of the valence band at A sites. For the majority spin states, the $d_{y^2-z^2}$ DOS is dominant. For the minority spin states, the $d_{t_{2g}}$, $d_{3x^2-r^2}$ and $d_{y^2-z^2}$ DOS's appear separately with energies from 0 to 4 eV. These peaks are slightly different from the LDA+ U result,³⁾ in which the partial DOS's of the majority spin states are overlapping with energies in the range of 2 to 6 eV. The LDA results are expected to be better, since it is known from other oxides¹⁴⁾ that the 3d DOS in Hartree-Fock approximation is modified by electron correlations to become close to that of the LDA.

Fig. 2. Density of states projected onto the d symmetry at A sites. The zero of energy is at the top of the valence band. The intensity of the t_{2g} symmetry is reduced to one-third of its actual value.

Figure 3 shows the DOS at A sites projected onto states of p symmetry. The PKE structure appears at energies between 0 ~ 5 eV with the intensity being roughly 1/20 of the main peak intensity. It originates from the 4p states mixing to the 3d states of neighboring Mn sites. As shown in the inset, it is classified into three regions a , b and c . For the majority spin states, only the p_x DOS has an appreciable intensity in region a , while the p_z DOS is dominating for the minority spin states. The former results from the mixing to the unoccupied $d_{z^2-x^2}$ states of Mn sites in the same $a-b$ plane (B_1 and B_3 in Fig. 1), while the latter (minority spin) comes from the mixing to the $d_{y^2-z^2}$ states (majority spin) of Mn sites above and below the considered plane (note that the magnetization direction is opposite in adjacent planes). In region b , the p_y DOS is most prominent for the minority spin states. It results from the mixing to the $d_{3y^2-r^2}$ state of Mn

sites in the same $a-b$ plane (B_2 and B_4 in Fig. 1). In region c , the p_z DOS is dominant for the majority spin states, while the p_x DOS is dominant for the minority spin states. The former results from the mixing to the $d_{y^2-z^2}$ state (minority spin) of Mn sites above and below the considered plane, while the latter results from the mixing to the $d_{z^2-x^2}$ (minority spin) of Mn site in the same $a-b$ plane (again B_1 and B_3 in Fig. 1). This PKE structure is consistent with the previous LDA+ U result,³⁾ although the details are different.

Fig. 3. Density of states projected onto the p symmetry at A sites. The zero of energy is at the top of the valence band. The inset shows the intensity in the pre-edge region.

The resonant X-ray scattering is described by a second-order process in which the photon is virtually absorbed and then emitted. The dipole transition corresponds to a transition from the 1s state to the p -symmetric states at Mn sites, while the quadrupole transition corresponds to a transition from the 1s state to the d -symmetric states. Since in the PKE region the d -symmetric DOS is much larger than the p -symmetric DOS, the quadrupole effect can be comparable in size with the dipole effect. In the followings we consider both possibilities. The scattering geometry is the same as the experimental configuration as regards the polarization, the Bragg angle θ and the azimuthal angle ψ .¹⁾ The condition $\psi = 0$ corresponds to the configuration in which the c axis is perpendicular to the diffraction plane. We consider only the scattering from polarization σ to π' , since the $\sigma \rightarrow \sigma'$ scattering has no AXS intensity.¹⁵⁾

The scattering amplitude $T_{\sigma \rightarrow \pi'}(\omega)$ at Mn sites is divided into dipole and quadrupole processes:

$$T_{\sigma \rightarrow \pi'}(\omega) = J_{\sigma \rightarrow \pi'}(\omega) + L_{\sigma \rightarrow \pi'}(\omega), \quad (1)$$

where

$$J_{\sigma \rightarrow \pi'}(\omega) = \sum_{\alpha\beta} (D^{\pi'})_{\alpha}^{\dagger} M_{\alpha\beta}(\omega) D_{\beta}^{\sigma}, \quad (2)$$

with

$$M_{\alpha\beta}(\omega) = \sum_j \frac{\langle 1s|x_\alpha|p_j\rangle\langle p_j|x_\beta|1s\rangle}{\omega - (\epsilon_j - \epsilon_{1s}) + i\Gamma}, \quad (3)$$

$$D^\sigma = \begin{pmatrix} -\sin\psi/\sqrt{2} \\ \sin\psi/\sqrt{2} \\ \cos\psi \end{pmatrix}, \quad (4)$$

$$D^{\pi'} = \begin{pmatrix} (\cos\theta - \sin\theta\cos\psi)/\sqrt{2} \\ (\cos\theta + \sin\theta\cos\psi)/\sqrt{2} \\ -\sin\theta\sin\psi \end{pmatrix}, \quad (5)$$

and

$$L_{\sigma\rightarrow\pi'}(\omega) = \sum_{\alpha\beta} (Q^{\pi'})^\dagger_\alpha N_{\alpha\beta}(\omega) Q^\sigma_\beta, \quad (6)$$

with

$$N_{\alpha\beta}(\omega) = \frac{k^2}{12} \sum_\ell \frac{\langle 1s|z_\alpha|d_\ell\rangle\langle d_\ell|z_\beta|1s\rangle}{\omega - (\epsilon_\ell - \epsilon_{1s}) + i\Gamma}, \quad (7)$$

$$Q^\sigma = \begin{pmatrix} \sin\theta\sin\psi \\ \frac{\sqrt{3}}{2}\cos\theta\sin2\psi \\ -\frac{1}{\sqrt{2}}(\cos\theta\cos2\psi + \sin\theta\cos\psi) \\ \frac{1}{\sqrt{2}}(\cos\theta\cos2\psi - \sin\theta\cos\psi) \\ \frac{1}{2}\cos\theta\sin2\psi \end{pmatrix}, \quad (8)$$

$$Q^{\pi'} = \begin{pmatrix} \cos2\theta\cos\psi \\ \frac{\sqrt{3}}{4}\sin2\theta(\cos2\psi - 1) \\ \frac{1}{2\sqrt{2}}(\sin2\theta\sin2\psi + 2\cos2\theta\sin\psi) \\ \frac{1}{2\sqrt{2}}(-\sin2\theta\sin2\psi + 2\cos2\theta\sin\psi) \\ \frac{1}{4}\sin2\theta(\cos2\psi + 3) \end{pmatrix}. \quad (9)$$

The incident and emitted photons have wave number $k \approx 3.3 \times 10^8 \text{ cm}^{-1}$, since the K-edge absorption energy is 6.552 keV. The ω represents the photon energy. The lifetime broadening width Γ of the $1s$ core hole is assumed to be 1 eV. Energies ϵ_{1s} , ϵ_j and ϵ_ℓ correspond to the core state $|1s\rangle$ and the excited p states, $|p_j\rangle$, and d state, $|d_\ell\rangle$, respectively. The dipole operators are defined as $x_1 = x$, $x_2 = y$ and $x_3 = z$, and the quadrupole operators are $z_1 = (\sqrt{3}/2)(x^2 - y^2)$, $z_2 = (1/2)(3z^2 - r^2)$, $z_3 = \sqrt{3}yz$, $z_4 = \sqrt{3}zx$ and $z_5 = \sqrt{3}xy$. We neglect the final-state interaction between the $1s$ core hole and the excited electron. The excited p electrons are so extended that for the dipole process their effect is expected to be small, but it may not be small for the quadrupole process due to the localized nature of the $3d$ states.

Using the relations $M_{11}^B(\omega) \simeq M_{22}^A(\omega)$, $M_{22}^B(\omega) \simeq M_{11}^A(\omega)$, $M_{33}^B(\omega) \simeq M_{33}^A(\omega)$ and $M_{12}^A(\omega) \simeq 0$, we obtain for the dipole transition the AXS amplitude,

$$J_{\sigma\rightarrow\pi'}^A(\omega) - J_{\sigma\rightarrow\pi'}^B(\omega) = -\cos\theta\sin\psi(M_{11}^A(\omega) - M_{22}^A(\omega)). \quad (10)$$

For the quadrupole transition, we introduce the local coordinate frame according to $x \rightarrow z$, $y \rightarrow x$, $z \rightarrow y$ at A sites, and $x \rightarrow y$, $y \rightarrow z$, $z \rightarrow x$ at B sites. Thereby the quadrupole operators are transformed such that $z_1 \rightarrow (-1/2)z_1 \pm (\sqrt{3}/2)z_2$, $z_2 \rightarrow (\mp\sqrt{3}/2)z_1 - (1/2)z_2$ (the upper and lower signs are for A and B sites, respectively). Keeping only the diagonal terms $N_{11}^A(\omega)$ and $N_{22}^A(\omega)$ in these local coordinate frames, we obtain for

the quadrupole transition the AXS amplitude,

$$L_{\sigma\rightarrow\pi'}^A(\omega) - L_{\sigma\rightarrow\pi'}^B(\omega) = \frac{3}{4}[\cos2\theta\cos\theta\cos\psi\sin2\psi + \frac{1}{2}\sin2\theta\sin\theta\sin\psi(\cos2\psi - 1)](N_{11}^A(\omega) - N_{22}^A(\omega)). \quad (11)$$

The $N_{11}^A(\omega)$ and $N_{22}^A(\omega)$ are proportional to the $d_{y^2-z^2}$ and $d_{3x^2-r^2}$ DOS's in the original coordinate frames. The $d_{t_{2g}}$ DOS does not contribute to the AXS intensity due to a cancellation between the amplitudes at A and B sites.

Since the main peak of the p -symmetric DOS gives rise to the real part of the PKE amplitude, the AXS intensity is enhanced by an interference between the tail of the main peak and the value brought about by the PKE DOS. Figure 4 shows the AXS intensity of $\sigma \rightarrow \pi'$ scattering corresponding to the $(1, 0, 0)$ reflection. The PKE intensity is approximately 1/100 of the main peak intensity, owing to the interference. The PKE structure consists of two peaks; the one around $\omega \sim 0.5$ eV originates from the p -symmetric DOS of the majority spin states in region a , while the other around $\omega \sim 3$ eV originates from the p -symmetric DOS of the minority spin states in regions b and c (see Fig. 3). The fact that the solid curves are different from the broken ones indicates an appreciable effect of the quadrupole transition.

Fig. 4. The AXS intensity of $\sigma \rightarrow \pi'$ scattering associated with the $(1, 0, 0)$ reflection for several azimuthal angles, as a function of the photon energy ω . The inset shows the overall spectra. Here $\omega = 0$ corresponds to the energy required for the transition from the $1s$ state to the state at the top of the valence band. The numbers attached to the curves represent the azimuthal angles.

Figure 5 shows the azimuthal-angle dependence of the

AXS intensity at $\omega = 3$ eV associated with the (1,0,0) reflection. As shown in the upper panel, the difference of the intensities with and without the effect of the quadrupole transition for some angles is negative. This is due to an interference between the effects of the quadrupole process and the dipole one. The effect of the quadrupole transition is one order of magnitude smaller than that of the dipole transition.

Fig. 5. Azimuthal-angle dependence of the AXS intensity of the $\sigma \rightarrow \pi'$ transition at $\omega = 3$ eV associated with the (1,0,0) reflection. The broken line represents the intensity coming from the dipole process. The upper panel shows the difference of the intensities with and without the quadrupole process. The scale of the ordinate is the same as in Fig. 4.

In summary, we have calculated the anomalous X-ray scattering intensity, using the KKR method based on the LDA. We have found a two-peak structure in the pre-K-edge region with an intensity approximately 1/100 of that of the main peak. This originates from a mixing of $4p$ states of Mn to $3d$ states of neighboring Mn sites. Therefore it is rather sensitive to the $3d$ states and the orbital order, though the relation is not a direct one. It seems dangerous to use a simple tight-binding model for describing the $4p$ states, since they are so extended and the mixing is mediated by oxygen sites situated between Mn sites. The results of the present paper suggest that the JT distortion has a secondary effect on the PKE structure. This contrasts with the main peak, which is generated by the Jahn-Teller distortion.^{3,4,5)} The quadrupole effect shows a special azimuthal-angle dependence through the interference with the dipole effect, but the effect is one order of magnitude smaller than the dipole effect.

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